THE EFFECT OF CATHODE COMPOSITION ON THE THERMAL CHARACTERISTICS OF LITHIUM ION CELLS

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ABSTRACT

The specific thermal capacity and heat dissipation rate for lithium ion cells containing $LiNiO_2$ and mixed oxide (75%$LiCoO_2$+ 25%$LiNiO_2$) as cathode materials are compared. The experimental measurements were made using a radiative calorimeter consisting of a copper chamber maintained at -168°C by circulating liquid nitrogen and enclosed in a vacuum bell jar. The specific thermal capacity was determined based on warm-up and cool-down transients. The heat dissipation rate was calculated from the values measured for heat radiated and stored, and the resulting values were corrected for conductive heat dissipation through the leads. The specific heat was 1.117 J/°C-g for the $LiNiO_2$ cell and 0.946 J/°C-g for the 75%$LiCoO_2$,25%$LiNiO_2$ cell. Endothermic cooling at the beginning of charge was very apparent for the cell containing 75%$LiCoO_2$,25%$LiNiO_2$ as the cathode. Exothermic heating began at a higher state of charge for the cell with the 75%$LiCoO_2$,25%$LiNiO_2$ cathode compared to the $LiNiO_2$ cathode cell. During discharge, the rate of heat dissipation increased with increase in the discharge current for both types of cells. The maximum heat dissipated at C/5 discharge was 0.065 W and 0.04 W for the $LiNiO_2$ and 75%$LiCoO_2$,25%$LiNiO_2$ cells, respectively. The thermoneutral potential showed variability toward the end of discharge. The plateau region of the curves was used to calculate average thermoneutral potentials of 3.698 V and 3.837 V for the $LiNiO_2$ cell and the 75%$LiCoO_2$,25%$LiNiO_2$ cell, respectively.

INTRODUCTION

This study was conducted to determine the specific thermal capacity, heat dissipation rates during charge and discharge, and thermoneutral potential of lithium ion cells, with the specific purpose of aiding future satellite programs in battery selection and sizing. In view of the interdependence of temperature and performance, the thermal behavior of batteries is of paramount importance in selecting the operating conditions (such as temperature, recharge ratio, and current density) and extending the life of the battery for aerospace missions. In addition, safety-related incidents such as that reported for the lithium ion battery manufactured for the PowerBook 5300 portable computer necessitate a proper understanding of thermal runway and venting of lithium ion batteries (1).

Various authors have examined the thermal phenomena of lithium ion batteries. For example, Botte *et al.* (1) reported on the role of carbon particle size in the heating rate during discharge, Hong *et al.* (2) discussed the heat rates obtained from calorimetric measurements, and Chen and Evans (3) presented a mathematical analysis indicating the absence of thermal runaway conditions during normal battery operation. The present study is an experimental evaluation of thermal characteristics using a radiative calorimeter.

CELL SELECTION

The cells selected for this study were provided to NASA Goddard Space Flight Center for an evaluation program. The $Li_xC/LiNiO_2$ (Cell A) and Li_xC/75%$LiCoO_2$, 25%$LiNiO_2$ (Cell B) cells were of the 18650 type and contained the same type of graphite as the anode material, the same kind of separator, and the same electrolyte composition. The cathode active material was the only variable in the design of these cells. The cells contained a plastic-insulated seal and a puncture diaphragm, in a nickel-plated can. Both cell types contained spirally wound electrodes of approximately the same dimensions.

CAPACITY AND VOLTAGE

As a first step in thermal analysis, the capacity and voltage behavior of the cells were determined. A constant-temperature chamber was used for capacity determinations. Charging and discharging were done galvanostatically, with termination voltages of 4.1 V and 2.5 V during charge and discharge, respectively . Figure 1 shows the voltage profiles for the two types of cells during charge at the C/5 rate at 25°C. The cell A, containing the $LiNiO_2$ cathode exhibited slightly higher voltage than the cell B,containing 75%$LiCoO_2$,25%$LiNiO_2$ as the cathode material. Figure 2 shows the voltage during discharge at C/5 for at 25°, 10°, and 0°C for the two types of cells. There are remarkable differences in the behavior of the two cell types. The cell containing $LiNiO_2$ exhibits greater capacity at all temperatures except 10°C and lower discharge voltage at all temperatures except 0°C. Cell B (75%$LiCoO_2$,25%$LiNiO_2$cathode) showed an anomaly in slightly higher capacity for 250 mA discharge compared to that at 125 mA discharge that was previously observed in our laboratory. Table I summarizes the capacity data at various temperatures and discharge rates for the two types of cells.

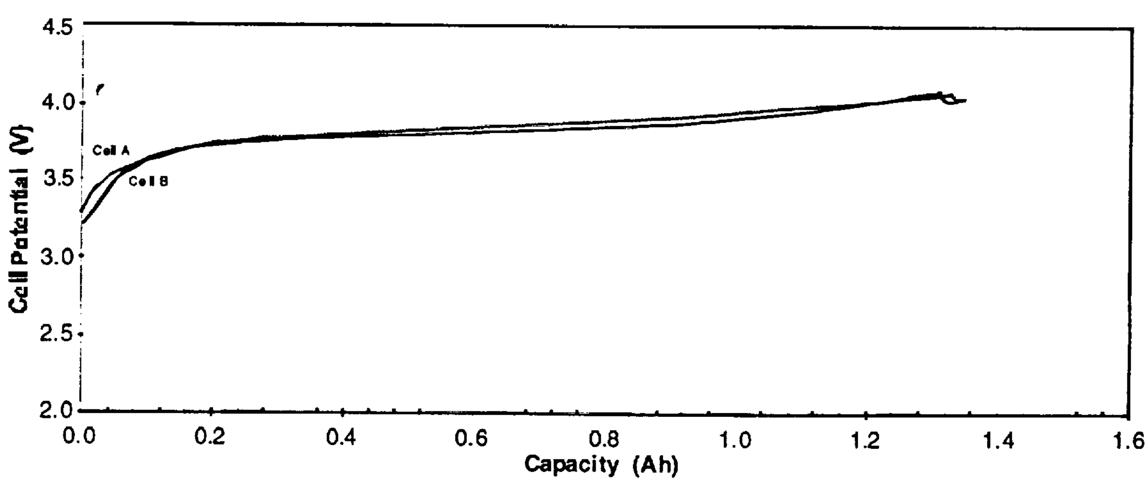

Figure 1. Voltage Profiles During Charge at 25°C
Cell A = $LiNiO_2$ Cathode
Cell B = 75%$LiCoO_2$,25%$LiNiO_2$ Cathode

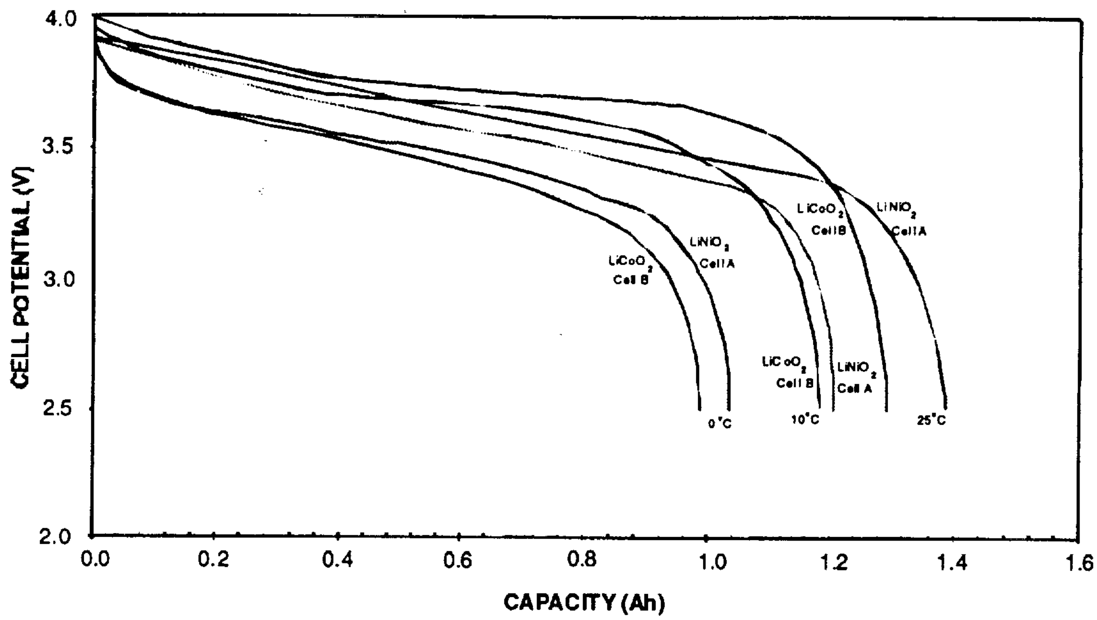

Figure 2. Potential Profiles During Discharge at C/5
Cell B = 75%$LiCoO_2$,25%$LiNiO_2$ Cathode
Cell A = $LiNiO_2$ Cathode

Table I. Capacity following C/5 rate of charge

Cycle No.	End-of-Charge Voltage (V)	Discharge Current (mA)	Temperature (°C)	Capacity to 2.5 V (Ah)*		Mid-discharge Voltage (V)	
				Cell B	Cell A	Cell B	Cell A
1	4.1	250	25	1.29	1.40	3.718	3.605
2	4.1	625	25	1.26	1.36	3.641	3.581
3	4.1	125	25	1.27	1.45	3.748	3.614
4	4.1	250	10	1.22	1.21	3.679	3.582
5	4.1	150	0	0.98	1.05	3.504	3.52

* Cell B contains a 75%$LiCoO_2$,25%$LiNiO_2$ cathode, and Cell A contains a $LiNiO_2$ cathode.

HEAT DISSIPATION

Heat dissipation during discharge, charge, and self-discharge of batteries is an important parameter, not only for the safe operation of the battery, but also for extending its cycle and calendar life. In addition, it is important to know whether the battery is susceptible to thermal runaway when the rate of heat generated exceeds the rate of heat dissipated. Another thermal condition that affects battery operation is the development of thermal gradients and hot spots, which greatly accelerate degradation of the electrolyte, anode, cathode, and separator. The thermal characterization of lithium ion cells is complex and difficult due to uncertainty regarding enthalpy values, reaction mechanisms, and side reactions.

A radiative calorimeter was used in this study to measure heat dissipation rates under transient conditions (4). The radiative calorimeter is ideally suited to determining heat rates in fractional watts because of its high sensitivity (0.002 W/°C for the radiative term, compared to a calorimetric constant of 1 W/°C for the conductive calorimeter). Heat leakage through the leads and sensing wires by conduction can be calculated and compensated. The term $mC_p\, dT/dt$ is involved in the calculations, and heat stored and heat dissipated are calculated separately.

CALORIMETER

The calorimeter is designed for radiative transfer of heat from the cell to its surroundings (4). It consists of a 0.5-m^3 copper chamber that is maintained at -168°C by circulating liquid nitrogen. The inside of the chamber is painted black, and the cell is suspended using a lacing cord. The calorimetric chamber is arranged in bell-jar-type vacuum chamber, and a vacuum of 10^{-5} torr is maintained.

In preparing the cell for calorimetry, great care was taken that it had a distinct radiating surface. A 2.54-cm-wide, 5-cm-long thermofoil heater tape was wrapped around the cell, and six thermocouples were installed at different areas of the cell. The thermocouple sensing wires, terminal leads, voltage sensing leads, and heater leads were bunched to create two wire bundles and insulated with multiple layers of aluminized Mylar. The exposed areas of the cell were also insulated with multiple layers of Mylar. Heat was applied to the cell through thermofoil heaters to raise its temperature significantly above that of the calorimetric chamber (-168°C). Thus, heat was radiated from the cell following the relationship:

$$Q_r = \varepsilon \sigma A (T_c^4 - T_s^4) \tag{1}$$

where

A	=	Area of the radiating surface
Q_r	=	heat radiated (W)
ε	=	emissivity
σ	=	Stefan-Boltzmann constant (5.6697×10^{-8} $W/m^2 K^4$)
T_c	=	temperature of the cell (K)
T_s	=	temperature of the calorimeter (-168°C).

Heat dissipated from the cell, Q_{diss}, can be expressed as

$$Q_{diss} = Q_h - Q_r - Q_{cond} - Q_s \tag{2}$$

where

Q_h	=	heater power (W)
Q_r	=	heat radiated (W)
Q_{cond}	=	conductive heat loss (W)
Q_s	=	$mC_p\, dT/dt$ (W).

where

m	=	mass of the cell (g)
C_p	=	thermal capacity (J/°C) of the cell
T	=	temperature of the cell (°C)
t	=	time (s).

To allow for heat loss and gain through the voltage sensing and power leads, heater power leads, and thermocouple leads, the conductive heat transfer from the cell through the leads was calculated by measuring the temperature difference at the beginning (cell surface) and end (point of exit from the calorimeter) of the wire bundle. Values (in watts) were calculated as follows:

$$Q_{cond} = hA\ (T_{cell} - T_{wire\ bundle})/l \tag{3}$$

where

Q_{cond}	=	heat transfer by conduction (W)
h	=	heat transfer coefficient of lead and wire materials
A	=	cross-sectional area (cm^2)
l	=	length of wires and leads (cm)
$T_{wire\ bundle}$	=	temperature of wire bundle (°C).

The calculated Q_{cond} was 0 0.01118 W/°C. The power applied to the cell heater was set at different values, and the corresponding cell temperatures were measured at steady state and at open-circuit voltage. The steady-state data were then plotted, and the following equations were derived by curve fitting:

$$Q_r = 1.5264 + 0.0173T_{avg} \qquad \text{LiNiO}_2 \text{ Calthode Cell} \tag{4}$$

$$Q_r = 1.675 \text{ X } 10^{-10}(273 + T_{avg})^4 \quad 75\%\ \text{LiCoO}_2,\ 25\%\text{LiNiO}_2 \text{ Cathode} \tag{5}$$

The thermal capacity the cells were determined based on the temperature transients during warm-up at a heater power of 1.92 W, and during cool-down using no heater power. The average cell temperature was converted to Q_{rad} using equation (4) for several time intervals, and Q_{cond} was calculated using equation (3). Thermal capacity was then calculated using:

$$mC_p = (Q_h - Q_r - Q_{cond})\ \mathrm{d}t\,/\,\mathrm{d}T \tag{6}$$

The thermal capacity of the 75% $LiCoO_2$,25% $LiNiO_2$ cathode cell was found to be 40.246 J/°C or 0.946 J/°C-g and that of the $LiNiO_2$ cathode cell using the same procedure was 50.822 J/°C or 1.117J/°C-g.

HEAT DISSIPATION DURING CHARGE

The cells were stabilized at a heater power of 1.912 W and charged at 250 mA until the potential reached 4.1 V, with concurrent measurement of temperature and heat dissipation rate. Figure 3 shows the variation in temperature for the two types of cells. The temperature of the cells leveled off in 2 hours with the cell containing the $LiNiO_2$ cathode exhibiting a higher temperature.

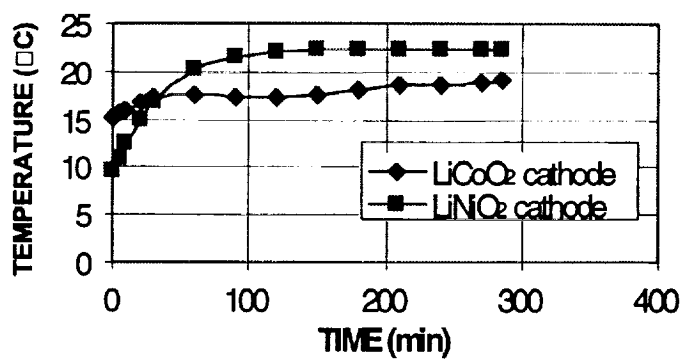

Figure 3. Variation of Temperature During Charge at C/5

. The variations in heat dissipation during charge are shown for the two types of cells depicted in Fig. 4. Thermal behavior is characterized by an initial rise in the heat rate, followed by endothermic cooling and then exothermic heating. The initial spike in heat dissipation is unique to Li-ion cells and it is attributed to a side reaction symbolized as:

$$2Li_xC_6 + yC_3H_4O_3 > yLi_2CO_3 + yC_2H_4 + 2Li_{x-y}C_6$$

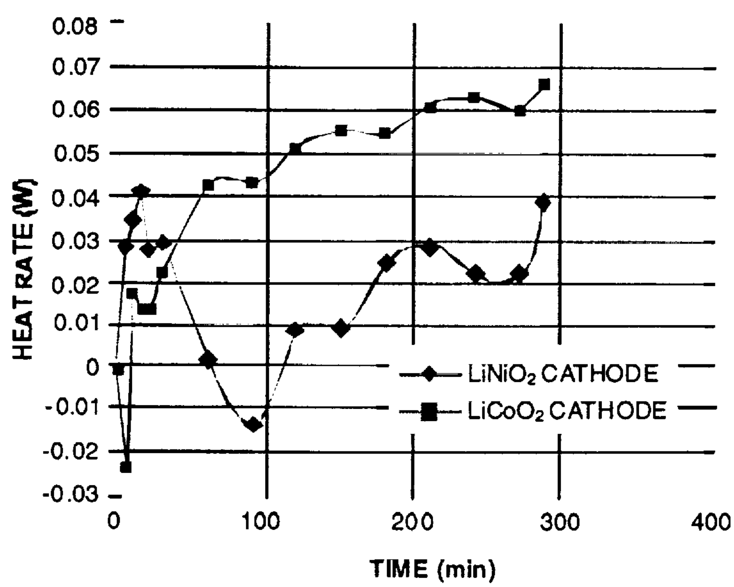

Figure 4. Variation of Heat Rate Duing charge at C/5

This reaction is one of the complex set of reactions that occur during the formation of the passive layer on the carbon anode (1). The reaction is exothermic, with a heat of reaction of -289 kJ/mol of lithium reacted.

The maximum endothermic rate was 0.015 W. Exothermic heating begins at a higher state of charge for the 75%$LiCoO_2$,25%$LiNiO_2$ cathode than for the lithiated nickel-oxide cathode. At the end of charge, the heat rate was 0.040 W for the cell containing 75%$LiCoO_2$,25%$LiNiO_2$ and 0.065 W for the cell containing $LiNiO_2$.

The charging reactions consist of deintercalation of lithium ions from the lithium cobalt-oxide cathode and intercalation into the graphite anode. The entropy change dominates the total heat dissipated during charge at C/5. The deintercalation is believed to be endothermic. Reactions at the carbon anode are not expected to be of any thermal consequence.

HEAT DISSIPATION DURING DISCHARGE

The rates of heat dissipation during discharge to a state-of-charge of 60% at C/5 for the two cell types are shown in Figure 5. The profiles show a rapid rise in the heat rate initially followed by a marginal decrease, and then an increase. The initial increase was also reported by Hong *et al.* (5). The $LiNiO_2$ cathode cell dissipated more heat than the 75%$LiCoO_2$,25%$LiNiO_2$ cathode cell. Figure 6 shows the variation in heat dissipation rates at various rates of discharge for the cell containing the 75%$LiCoO_2$,25%$LiNiO_2$ cathode. As expected, the dissipation rate increased with increased rate of discharge. The heat rate during C/2 discharge was 0.28 W, or 11.21 W/cm^3, and at C rate it was 0.55 W for the 75%$LiCoO_2$,25%$LiNiO_2$ cell.

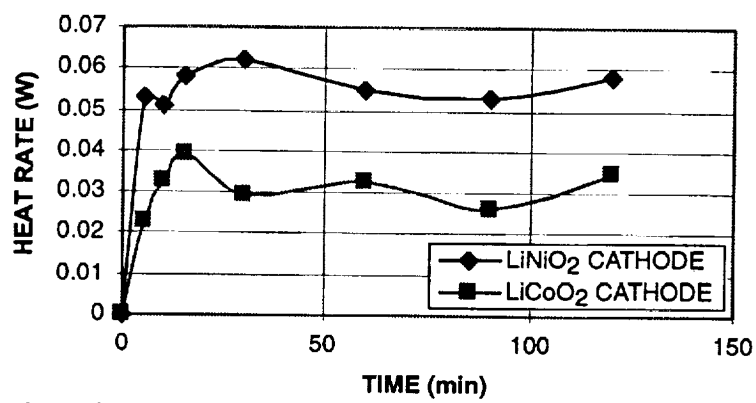

Figure 5. Variation of Heat Rate During Discharge at C/5

The most striking feature of the heat dissipation is the initial maximum, followed by a reduction in the heat rate. The expected behavior was a gradual increase in the heat rate as discharge is continued, followed by a very rapid rise toward the end of discharge.

The total heat generated in the cell has three components: entropic, ohmic, and electrochemical polarization. The heat rate attributable to electrochemical polarization is expected to be much lower at the beginning of discharge, and to increases gradually. The entropic contribution is a function of the chemical state of the participants in the main cell reaction. Ohmic heating is not expected to change significantly during discharge, and

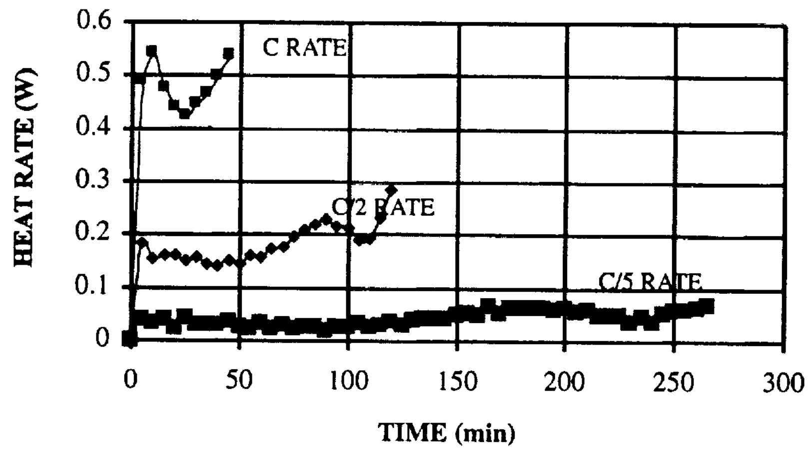

Figure 6. Variation of Heat Rate at Various Rates of Discharge

is expected to be lower than the heat, due to entropy change. It is suggested that the initial increase in heat rate during discharge is entropy-related. The main cell reaction is delithiation at the cathode, which is believed to be exothermic. The structure of Li_xCoO_2 and $LiNiO_2$ has been studied, and they are believed to undergo reversible phase transitions due to switching between trigonal and monoclinic crystal symmetries) (5). Bernardi, Pawlikowski, and Newman (6) reported that phase changes contribute to the total enthalpy, and that such changes are included as a separate term in addition to reaction enthalpy and the enthalpy of mixing. The suggested explanation for the initial increase, followed by lowering, in the heat rate curve is a phase change in the cathode active material.

THERMONEUTRAL POTENTIAL

The heat dissipation data obtained in this study can be used to calculate the thermoneutral potential, using the following equation:

$$E_H = -Q_{diss}/I + E_L \qquad (6)$$

where E_H is thermoneutral potential, I is discharge current, and E_L is cell voltage during discharge. This equation assumes that the discharge reaction is 100-percent efficient.

Figure 7 shows the variation in calculated E_H values during charge and discharge for the cell containing $75\%LiCoO_2$,$25\%LiNiO_2$ as cathode. The three curves that show the variation of E_H during discharge at C/5, C/2, and C exhibit a plateau in the mid-discharge region. The curve obtained during charge at C/5 shows very stable values for E_H. The calculations suggest an average value of 3.837 V for E_H, as given in Table II.

The calculated value for the $LiNiO_2$ cathode cell, using the charge at C/5 data, is 3.554 V, and that using the discharge data is 3.843 V. The average value is 3.698 V

The values for thermoneutral potential obtained in this study are in agreement with the negative temperature coefficient for the voltage reported in the literature (2). It can be inferred from the thermoneutral potential that:

- The products of the discharge reaction are more ordered than the reactants.
- Zero heat generation and endothermic cooling occur at some point during charge.
- Battery discharge will generate heat.
- Open-circuit potential will be less than thermoneutral potential at all temperatures.

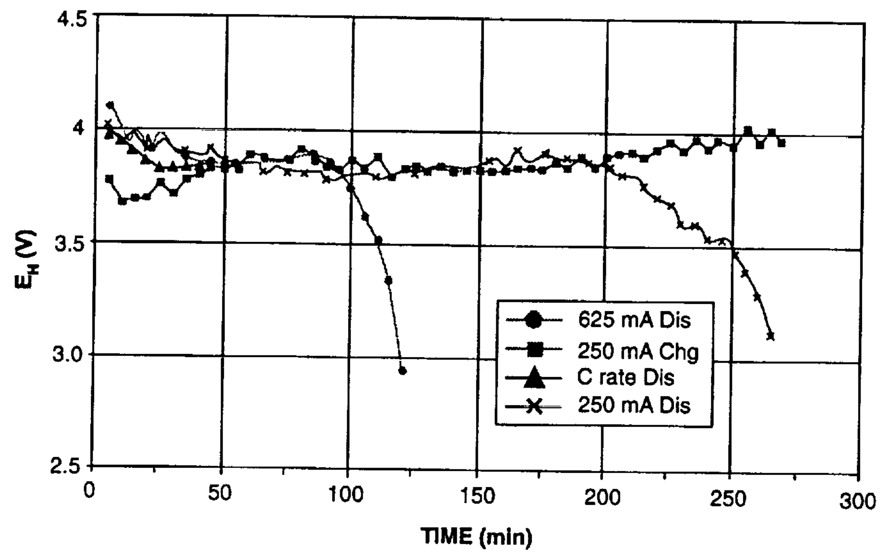

Figure 7. Variation of E_H During Discharge and Charge for the $LiCoO_2$ Cell

Table II. Calculated values for E_H (75% $LiCoO_2$, 25% $LiNiO_2$ cell)

Test Regime	Value of E_H
Discharge at 1A	3.8073
Charge at C/2	3.8109
Discharge at C/2	3.8037
Charge at C/5 at 5°C	3.8456
Charge at C/5 at 18°C	3.8726
Discharge at C	3.8829
Discharge at C/5 at 5°C	3.8357
Average	3.8369

Ordinarily, thermoneutral potential can be used to calculate heat dissipation under various operating conditions, based on known voltage profiles during charge and discharge. The heat dissipation values so obtained can be used to construct a thermal map of the cell.

CONCLUSIONS

$LiNiO_2$ cathode cell yielded a higher capacity at all temperatures whereas the 75% $LiCoO_2$, 25% $LiNiO_2$ cathode cell showed a higher mid-discharge voltage at all temperatures except at 0°C The specific heats were 1.117 and 0.946 J/°C-g for the $LiNiO_2$ and 75% $LiCoO_2$,25%$LiNiO_2$ cathode cells, respectively. The cells showed endothermic cooling initially during charge followed by exothermic heating. In general, $LiNiO_2$ cathode cell dissipated more heat on charge and discharge and the onset of exothermic heating occurred at a lower state-of-charge. The heat dissipated during discharge increased with the rate of discharge. At C/2 rate of discharge (which is considered medium rate), the heat dissipated was 11.2 mW/cm^3 for the cell containing 75%$LiCoO_2$,25%$LiNiO_2$ as the cathode. The heat dissipation profiles for both the cell types during discharge were characterized by inflections, unlike what has been observed for Ni-Cd and Ni-H_2 cells. Thermoneutral potentials of 3.837 V for the 75% $LiCoO_2$,25%$LiNiO_2$ cathode and 3.698V for the $LiNiO_2$ cathode cell were obtained. These proposed values can explain the endothermic cooling during charge and the negative temperature coefficient for cell voltage. The results of this study suggests that the cathode of the lithium ion cell influences the thermal behavior of the cell..

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